University of Technology, Sydney

Spectroscopic Studies of Hydrogen Dopants in ZnO Crystals

by

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I, Laurent Olivier Lee Cheong Lem, declare that this thesis titled, 'Spectroscopic Studies of Hydrogen Dopants in ZnO Crystals' and the work presented in it are my own. I confirm that:

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Abstract

ZnO is a semiconductor with a direct band gap of 3.37 eV and an exciton binding energy of 60 meV at room temperature. These properties make it an attractive material for optoelectronic devices across a wide range of applications. Significant obstacles preventing the wide scale usage of ZnO include the lack of reliable *p*-type doping and high uncertainty surrounding the nature of its defects. Moreover, as-grown ZnO is intrinsically *n*-type and it is thought that hydrogen is the cause for the high *n*-type character.

The aim of this thesis is therefore to elucidate the role of hydrogen with respect to the optical and electrical properties of ZnO as well as its interaction with native defects and impurities.

During this work, hydrogen was introduced in ZnO single crystals through an RF plasma source. Hydrogen incorporation was confirmed by XPS measurements which showed an increase in hydrogenated oxygen states. Hydrogen also modified the near-surface region of the crystals only and not the bulk.

Hydrogen doped ZnO showed significant increases in the carrier concentration as well as in the near band edge (NBE) luminescence. This is attributed to hydrogen introducing new shallow donors. The green luminescence, whose origin is attributed to V_{Zn}, was quenched after hydrogen incorporation, indicating formation of neutral V_{Zn}-H_2 complexes. The yellow luminescence in the as-received crystal is identical to that in Li doped ZnO and was assigned to recombinations involving Li_{Zn}.

Hydrogen doped ZnO also exhibits a negative thermal quenching (NTQ) of the NBE luminescence where the intensity of the luminescence increases with increasing temperature. Q-DLTS measurements detected new electronic states being created following hydrogen incorporation. A model involving the H-related state

at 11 meV releasing electrons to form free excitons is proposed to explain the NTQ behaviour.

XANES studies of H-doped ZnO showed that hydrogen interacted with oxygen states only but not zinc. This suggests that most of the hydrogen dopants introduced by plasma sit at the oxygen anti-bonding site.

The recombination kinetics of the various luminescence was investigated. While the kinetics of the NBE luminescence followed the expected behaviour for excitonic type recombination, the green and yellow luminescences showed high temperature dependencies and is explained in terms of different recombination mechanisms.

Finally, it was found that hydrogen is stable under normal SEM excitation conditions.

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List of Publications

Refereed Journal Publications

Lee Cheong Lem, L., Ton-That, C., and Phillps, M.R. Distribution of visible luminescence centers in hydrogen-doped ZnO, *Journal of Material Research*, 26(23):2912, 2011.

Oral Presentations

Lee Cheong Lem, L., Ton-That, C., and Phillps, M.R. Investigations of hydrogen dopants in H-doped ZnO.
Australian Microbeam Analysis Society XII, Sydney. February 2013.

Lee Cheong Lem, L., Ton-That, C., and Phillps, M.R. Temperature dependence of cathodoluminescence of hydrogen doped zinc oxide.
ACCM 22 / APMC 10 / ICONN 2012, Perth, February 2012.

Lee Cheong Lem, L., Ton-That, C., and Phillps, M.R. Distribution of green and yellow luminescence centres in H-doped ZnO.
Australian Microbeam Analysis Society XI, Canberra. February 2011.

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A^0X	Neutral acceptor bound exciton
AFM	Atomic force microscopy
ASF	Atomic sensitivity factor
BX	Bound exciton
C-DLTS	Capacitance-based deep level transient spectroscopy
CB	Conduction band
CCD	Charge-coupled device
CVD	Chemical vapour deposition
CL	Cathodoluminescence
D^+X	Ionised donor bound exciton
D^0X	Neutral donor bound exciton
DAP	Donor-acceptor pair
DFT	Density functional theory
DLE	Deep level emission
DLTS	Deep level transient spectroscopy
DRCL	Depth-resolved cathodoluminescence
EPR	Electron paramagnetic resonance
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
FX	Free exciton
IMFP	Inelastic mean free path
LED	Light emitting diode
LO	Longitudinal optical
LVM	Local vibration mode
NBE	Near band edge

PL	Photoluminescence
Q-DLTS	Charge based deep level transient spectroscopy
sccm	standard cubic centimetres per minute
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
TES	Two-electron satellite
UV	Ultra-violet
UV-Vis	Ultra-violet visible
VB	Valence band
XANES	X-ray absorption near edge spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray diffraction